Unlocking Biomass Energy: A Computational Study on Cellulose Recalcitrance

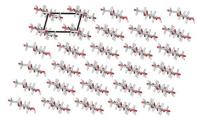
Giovanni Bellesia, T-6/CNLS; Ramakrishnan Parthasarathi, T-6; Antonio Redondo, T-DO; Shishir Chundawat, Bruce Dale, Great Lakes Bioenergy Center; S. Gnanakaran, T-6 Cellulose, an abundant component of lignocellulosic biomass, is self-assembled in plant cell walls as crystalline nanofibers. It can be hydrolyzed to monomeric glucose that can eventually be converted to biofuels (e.g., alcohols, alkanes) via microbial fermentation or chemical catalysis. The degradation of cellulose polymers to sugar monomers is currently an inefficient and expensive process. We used multiresolution computer simulations to investigate the molecular origin of cellulose recalcitrance to degradation. In particular, we focused on two cellulose crystalline forms that display different degrees of recalcitrance to degradation: cellulose I-beta (the natural crystalline form of cellulose) and the less recalcitrant cellulose III(I) obtained from cellulose I-beta by treatment with liquid ammonia.

Fig 1. Cellulose I-beta and III(I) crystal structures.

Cellulose IB

مېلېلىخ مېلېلىكى مېلېلىك مېلېلىك مېلېلىكى مېلىكى مې

Cellulose III



ne way to greatly improve the enzyme degradation process of crystalline cellulose fibrils to glucose is to convert the naturally occurring crystalline form of cellulose (cellulose I-beta) to a different crystalline form named cellulose III(I) (see Fig. 1). The conversion

process from crystalline cellulose I-beta to cellulose III relies on a chemical treatment based on anhydrous liquid ammonia. Recent experiments show that the enzymatic degradation rate is two to five times greater in cellulose III(I) than in cellulose I-beta [1].

We performed a set of extensive fully-atomistic molecular dynamics (MD) simulations to 1) gain a detailed understanding of the main structural and hydration differences between cellulose I-beta and cellulose III-I, and 2) relate these differences to the different enzyme degradation rates in these two cellulosic substrates [1]. Our MD simulations revealed substantial differences in the structural stability, surface properties, and hydration between cellulose I-beta and cellulose III(I) fibrils. These results helped greatly in explaining the molecular foundations of crystalline cellulose stability. In particular, the comparative computational analysis of both the crystalline core and the solvent-exposed surface of the cellulose I-beta and III(I) fibrils identified key structural and molecular features in cellulose III(I) that can explain its lower recalcitrance and its enhanced hydrolysis rates [1].

Additional MD simulations were instrumental in providing the first detailed, mechanistic model for the interaction of liquid ammonia with native cellulose and for the consequent structural crossover to cellulose III(I) [2]. We observed the rapid formation of an extended hydrogen-bond (HB) network between liquid ammonia and the cellulose molecules on the surface of the fibril. This newly formed HB network induces a major shift in the conformation of the cellulose chains within the crystalline fibers and drives a structural crossover from cellulose I-beta to a new crystalline structure compatible with both the ammoniacellulose I complex and cellulose III(I). A pictorial view of the structural crossover is given in Fig. 2. Our simulations reveal that significant changes in both the structural and hydration properties of the cellulose fibril happen prior to ammonia percolation and suggest rational ways to improve existing cellulose chemical pretreatments.

In a subsequent study, we combined classical MD simulations and quantum calculations to study the details of the interplay between hydrogen bonding and stacking interaction, as well as their role in the stabilization of crystalline cellulose I-beta and cellulose III fibrils [3]. The results demonstrate that individual HB interactions are stronger in cellulose I-beta than in cellulose III(I). However, the total HB contribution to stabilization is larger in cellulose III(I) due to the highly cooperative nature of the intersheet HB network. In addition, a significant contribution to the stabilization of cellulose I-beta from cooperative stacking interactions was observed. On the one hand, these results serve as a first attempt to quantify the interplay between HB and stacking interactions in cellulose. On the other hand, the results also suggest that both HB and stacking interactions need to be taken into account when designing novel chemical pretreatments and enzymes for improved catalysis of cellulosic biomass for biofuel production.

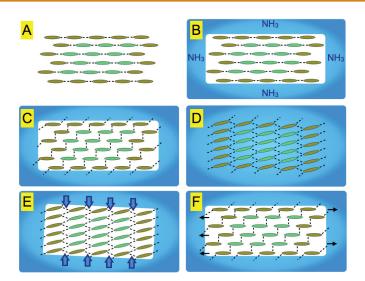


Fig. 2. Mechanistic model for the structural crossover from cellulose I-beta to cellulose III(I).

Finally, we introduced a generic coarse-grained molecular model for crystalline cellulose whose relevant degrees of freedom have been identified from the analysis of our fully atomistic MD simulations (see Fig. 3). The model provides a simple explanatory framework for structural transitions in crystalline cellulose in general, and for the transition from cellulose I-beta to cellulose III(I) in particular, where the search for optimal spatial arrangement of the cellulose chains appears to be more important than the chemical details of the cellulose crystals. In terms of catalytic

cellulose deconstruction for biofuels production, the model connects the lower recalcitrance of cellulose III(I) (when compared to cellulose I-beta) to higher free energy and to overall larger structural flexibility. The model suggests that the experimental strategies with the greatest chance of succeeding as effective chemical treatments for cellulose are those based on chemical compounds that specifically interfere with the energetics of the intersheet distance (the distance between neighboring horizontal sheets in cellulose fibrils—see Fig. 1) and compounds that expand cellulose I-beta via alteration of an internal rotational degree of freedom have the most chance of succeeding as effective chemical treatments for cellulose [4].

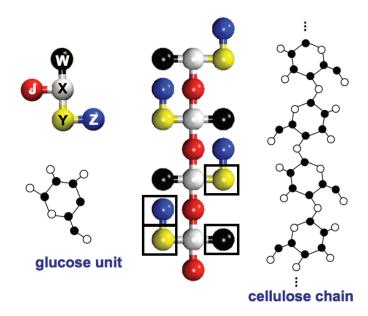


Fig. 3. Simplified geometry of our generic coarse-grained model for crystalline cellulose. Each glucose monomer (left) is represented by five beads: two for the backbone (X and J; white and red, respectively) and three for the side chains (Y, W and Z; yellow, black and blue, respectively).

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